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Ion irradiation-induced decomposition of Al + 4 wt. % Cu supersaturated solid solution

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Abstract. The decomposition process of the model precipitation-hardening Al + 4 wt. % Cu supersaturated solid solution induced by Ar⁺ ions irradiation. Using X-ray diffraction, high-resolution electron microscopy methods and microhardness measurements, it was established, that, already at low temperatures ($T < 60$ °C), ion irradiation causes accelerated decomposition of solid solution, with precipitation of θ' and θ -phase particles at a depth greatly exceeding the Ar⁺ ions projected range.

1. Introduction

Many experimental facts [1-12] gathered in the course of studying different properties and microstructure of ion-implanted materials testify to the fact that the effect of accelerated ion beams on materials is not limited to the ions penetration zone, but extends to much greater distances.

The terms “long-range action” and “long-range effects” as applied to the bombardment of solids with accelerated ions relate to the experimental facts of changes to the structure and properties of materials at depth L , which is much in excess of the mean projected range R_p of ions. It was found [6, 7, 9-12] that the maximum response to the ion irradiation as well as the most extended impact zone is observed for metastable media with a high stored energy.

It would be interesting to find out the extent of these phenomena (i.e., whether such processes are initiated under irradiation with accelerated ions in all or at least in the majority of metastable materials). Investigation of alloys displaying various types of structural phase [6, 7] and intra-phase transformations caused by ion irradiation deserves attention. This relates in particular to the formation of new phases by diffusion [7, 9] and diffusion-free mechanisms [4, 6], including details of the initial stages of transformation, e.g., irradiation-induced disperse phase nucleation and precipitation.

The present paper describes experimental investigations of the effect of irradiation with Ar⁺ ions on the process of decomposition of a supersaturated solid solution on example of the Al + 4 wt. % Cu precipitation hardening alloy.

As is known, decomposition of this supersaturated solid solution proceeds in several stages, with formation (1) of coherent (with the initial matrix) Guinier-Preston zones (ZGP); (2) of coherent precipitates of the metastable θ'' -phase; (3) of partially coherent particles of the θ' -phase; and (4) of incoherent particles of the stable CuAl₂ θ -phase [14]. The described sequence of phase transformations in the course of decomposition is responsible for primary strengthening (and following softening) of



this alloy. Significant strengthening at natural and artificial aging results from the formation of *ZGP*s and intermediate metastable θ'' and θ' -phases impeding the movement of dislocations. The subsequent stages, i.e., loss of coherence between the matrix and the metastable phase precipitates and formation and coagulation of stable phase precipitates, cause loss of strength.

2 Experimental

Samples of a Al + 4 wt. % Cu alloy in the form of 100 μm -thick plates were irradiated with Ar^+ ions ($E = 20 \text{ keV}$, $j = 160 \mu\text{A}/\text{cm}^2$) after their quenching in water from 520 °C in order to obtain the supersaturated solid solution state. Irradiation with a continuous argon ion beams was carried out using a reflex-glow-discharge based ion source [14]. The sample was fixed to a copper collector with a heat-conducting compound for better heat removal. The sample temperature during irradiation was kept under control and never exceeded 60 °C, even under the longest (30 min) exposure to the ion beam. The ion implantation parameters are given in the Table 1.

Table 1. Irradiation parameters of Al + 4 wt. % Cu alloy samples.

Ord. No.	Ion beam parameters				Time, min	Fluence, cm^{-2}
	Ar^+ mass, a.m.u.	j , $\mu\text{A}/\text{cm}^2$	E , keV	R_p , nm		
1	39.962	160	20	22.5	0.017 (1 s)	10^{15}
2					0.33 (20 s)	$2 \cdot 10^{16}$
3					1	$6 \cdot 10^{16}$
4					5	$3 \cdot 10^{17}$
5					15	$9 \cdot 10^{17}$
6					30	$1.8 \cdot 10^{18}$

To investigate the structural-phase state and the microplastic resistance of the samples before and after Ar^+ ion irradiation, the following methods were used: X-ray diffraction analysis, high-resolution electron microscopy (HREM), Vickers microhardness and kinetic microhardness tests.

The X-ray diffraction analysis in order to determine the lattice spacing was carried out using the DRON-4-07 diffractometer and $\text{Cu}_{K\alpha}$ radiation. The electron microscopy study was performed with the help of a Philips CM-300 transmission electron microscope at an acceleration voltage of 300 kV.

The *microhardness test* at 40 g load was carried out using the Neophot microscope (the indenter penetration depth was between 6-8 μm). Besides, measurements of *kinetic microhardness* of irradiated samples were carried out by continuous indentation under a 5 g load in the Shimadzu DUH-2002 instrument. Continuous automatic recording of parameters in the course of indentation (such as load on indenter, depth of its penetration into material and duration of loading) allows correct measurements to be made of microplastic properties of thin surface layers of materials as well as of films and coatings at small and super small loads (0.1-5.0 g). The indenter penetration depth under a 5 g load was approximately 2-3 μm .

3 Results and discussion

At the lowest fluence $D = 1 \cdot 10^{15} \text{ cm}^{-2}$ (the irradiation time is 1 s), the greatest *increase* in microhardness is observed, as compared with the initial quenched state (Figure 1 a, b). With further increase of the irradiation dose, microhardness gradually *decreases*.

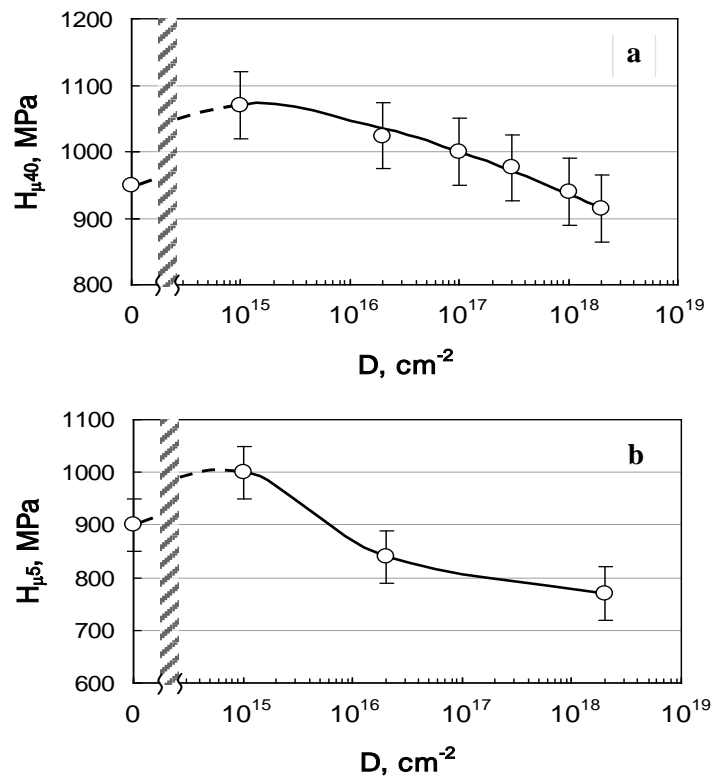


Figure 1. Changes in microhardness $H_{\mu,40}$ (a) and $H_{\mu,5}$ (b) of the Al + 4 wt. % Cu alloy in dependence on Ar⁺ ion irradiation dose.

Comparison of the results obtained under different loads shows that the *relative* changes in microhardness caused by irradiation are more pronounced under smaller load. This points to the fact that the degree of radiation-induced decomposition of the supersaturated solid solution (proved later with the X-ray lattice parameter measurements and XTEM examinations) at any *given* fluence is higher near to the irradiated surface. However, changes in microhardness under 40 g load (indenter penetration 6-8 μm) are also quite significant and testify that the supersaturated solid solution decomposes not near the irradiated surface only, but also at a depth many times exceeding the ions projected range.

The X-ray analysis data show an increase in the solid solution lattice parameter (Figure 2), which testifies to the fact that already at small irradiation doses ($\sim 10^{15}$ - 10^{16} cm⁻²) and low temperatures (< 60 °C) solid solution decomposition goes on with precipitation of second-phase particles which are observed after thermal annealing at a temperatures exceeding 150-200 °C. It should be noted that the X-ray diffraction method reflect the structural state over the ~ 50 μm thick surface layer [15]. Heating of a quenched sample in oil up to 60 °C and exposure during 30 min (reproducing the target heating mode under high-dose irradiation) causes no changes in the microhardness and the lattice parameter.

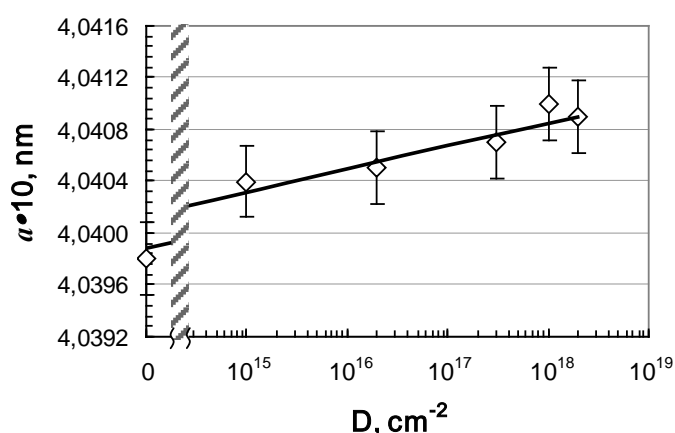


Figure 2. Changes in the lattice parameter a of the Al + 4 wt. % Cu alloy in dependence on Ar^+ ion irradiation dose.

Cross-sectional transmission electron microscopy investigations (XTEM) confirmed that ion irradiation causes decomposition of the solid solution with formation of θ'' -, θ' - and θ -phase particles. The microstructure of a sample after Ar^+ irradiation to a fluence of $2 \cdot 10^{16} \text{ cm}^{-2}$ is shown in Figure 3. The electron microscope images display a contrast from fine plate-shaped particles parallel to $\langle 001 \rangle_{\text{Al}}$ (Figure 3 a). To identify the type of the formed particles, the electron diffraction patterns of individual regions and high-resolution images (Figures 3 b-d) were analyzed. The values of interplanar spacings for planes $\{001\}_{\theta''}$, $\{101\}_{\theta'}$ and $\{200\}_{\theta}$ determined by Fourier transformation (0.75, 0.3 and 0.34 nm, respectively) are in satisfactory agreement with the known data (0.77, 0.3, and 0.33 nm) [13].

The investigated layer depth (in the cross-sectional image) was $\sim 1000 \text{ nm}$, and the whole volume of this layer contained the θ -, θ' - and θ'' -phase precipitates whereas the mean *projected range* R_p for Ar^+ ions, as calculated with the use of the TRIM method, being 22.5 nm only (see Table 1).

Precipitates of the stable θ -phase prevail near the irradiated surface, while the dominating θ' -phase is observed mainly at a larger depth. The extent of the zone of θ -phase (and particularly of θ' -phase) precipitation is, according to data of electron microscopy, microhardness tests and X-ray diffraction, at least two-three orders of magnitude greater than the indicated above ions projected range of 20 keV Ar^+ ions in Al + 4 wt. % Cu alloy.

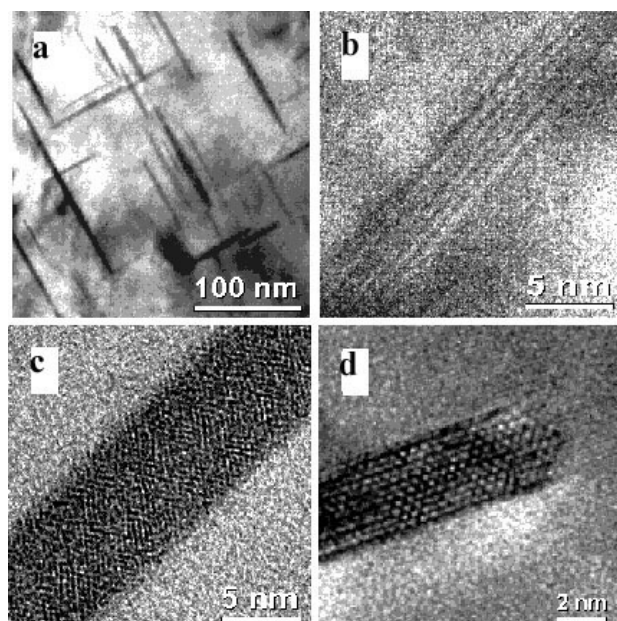


Figure 3. Results of electron-microscopic examination of cross-section samples irradiated with Ar^+ ions at $2 \cdot 10^{16} \text{ cm}^{-2}$ (exposure time 20 s, $j = 160 \mu\text{A}/\text{cm}^2$): precipitates of θ'' -, θ' - and θ -phase (a) and their HREM images (b, c, d).

The process of phase ageing manifests itself by the data of microhardness and lattice parameter measurements already at the fluence of $1 \cdot 10^{15} \text{ cm}^{-2}$, which corresponds to just 1 s of irradiation. This allows us to doubt the diffusion nature of the observed changes.

According to [12], radiation-stimulated (radiation-enhanced) migration processes are capable of just a several times increase of the depth of ions penetration into the material. So, thermostimulated and radiation-stimulated diffusion at $T = 500$ and 700 °C during 2 h increases the depth of Sb^+ (50 keV) ions penetration in silicon by approximately 50 to 100 nm. In our case, irradiation during only 20 s to a fluence of $2 \cdot 10^{16} \text{ cm}^{-2}$ at $T < 60$ °C, causes, according to direct XTEM data, decomposition of Al + 4 wt.% Cu solid solution in a zone of the order at least 1000 nm deep. In view of microhardness and lattice parameter measurements this rating may be increased to $(10^2\text{-}10^3)R_p$.

A multiple increase in the exposure depth and the rate of solid solution decomposition can be explained by the radiation-dynamic action of accelerated ions [10, 11, 16]. The essence of this effect is that the nanosized regions of atomic displacement cascades (Thermal Spikes [17, 18]) are zones of explosive energy release. The temperature of the cascade regions, which are thermalized within a time of the order of 10^{-12} s, may reach, according to Monte Carlo and molecular dynamics calculations, 5000-6000 K and even higher values.

Experimental proof of the formation of such extremely heated regions [18] has recently been obtained from the analysis of the emission spectra of metal targets (Fe, Zr and W) in the course of ion irradiation. Estimated temperatures are close to the simulated data.

The rapid heating of these regions and pressure boosting give rise to post-cascade shock waves. The pressure at the front of shock waves may exceed not just the real, but also the theoretical yield point of condensed matter [11, 18]. For comparison, the characteristic time of explosive energy release in a nuclear and in a chemical explosion is $\sim 10^{-8}$ and 10^{-5} s, respectively.

As it was shown in [7, 9, 11], the structural and phase transformations in metastable media with increased stored energy cover macroscopic volumes of the material and occur with high rates (often within several seconds of exposure) at rather small fluences ($D = 10^{15}\text{-}10^{16} \text{ cm}^{-2}$) and at reduced (by 150-200 K) temperatures compared to similar thermoactivated processes.

Radiation jolting of material with post-cascade waves may bring down the effective energy of diffusion activation [11] due to propagation in the volume of post-cascade shock waves. On the base of analysis of theoretical models [10, 11] it was shown that, in *metastable media*, such waves may become *unattenuating* (or slowly attenuating) at the expense of the energy liberated by structural-phase transformations at their front.

Metastable media with high stored energy, including supersaturated solid solutions as it has been shown by the present investigation, cold-worked materials [11] and alloys disordered by quenching or plastic deformation [7, 11], undergo maximum influence. Ion irradiation initiates fast-going (self-propagating into the depth of the material) processes transforming such media into the states with lower free energy. As a rough analogy, we may refer to the effects of explosive crystallization of supercooled liquid and decomposition of a supersaturated water solution as a result of impact or shaking.

The processes of phase formation/dissolution [11], atomic ordering and delamination [6, 7, 10], recrystallization of cold deformed materials [9, 11] (accompanied with explosive transformation of dislocation structure, with formation of point defects and activation of grain boundaries) and some others effects take place at anomalously low temperatures (100-200 °C below of similar thermostimulated processes).

The results of the investigation performed concerning *acceleration* of the processes of metastable medium transformation under irradiation, *bringing down* the temperature of phases precipitation, significant *increase* of the process depth (as compared with the ions penetration depth) are in agreement with the trends found in the available studies and supplement them with concrete actual data relating to the Al + 4 wt. % Cu system. The obtained data may be explained within the framework of the above mentioned approach.

4 Conclusion

Thus, it was established that irradiation of an Al + 4 wt. % Cu supersaturated solid solution with Ar⁺ ions strongly (at least 10³ times) accelerates its decomposition, ensuring precipitation of intermediate θ' , θ'' and equilibrium θ phases, taking place already at low temperatures (at which, in the course of usual heating, only the zonal stage of aging occurs, and even that requires long-term exposure). At that, the depth, at which phase precipitation proceeds, exceeds the ions penetration depth by at least two-three orders of magnitude (which follows from analysis of the microhardness, electron microscopy, and X-ray diffraction data).

In view of the real difficulties of explaining the fast processes of ageing of alloy Al + 4 wt. % Cu in the course of ion bombardment at *anomalously low* temperatures and at an *anomalously large* depth of (10²-10³) R_p within the scope of traditional migration models, the authors, with account for the earlier performed research [7, 10, 11], come out with a suggestion about a significant role of alternative mechanisms of radiation-dynamic nature.

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